

Effects of ultrasound time on the properties of methylcellulose-montmorillonite films

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Received: 27 September 2016 / Accepted: 11 February 2017 / Published online: 21 February 2017
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Abstract Methylcellulose-montmorillonite films were prepared via solvent casting method. The effects of different ultrasound times (0, 15, 30, 45, 60, and 75 min) on the properties of methylcellulose-montmorillonite films were evaluated. Fourier transform infrared and X-ray diffraction were applied to investigate and prove the effects of ultrasound time. The films were characterized by mechanical properties, opacity, water vapor permeability, yellowness index, and color. Ultrasound time significantly affected the characteristics of the films, except for elongation. Maximum tensile strength, opacity, YI , and b^* as well as minimum L^* and water vapor permeability were related to 60 min. The results from X-ray diffraction and Fourier transform infrared verified the effects of sonication time on the films properties, especially for 60 min. The Fourier transform infrared spectrum related to 60 min had more new and sharper peaks. The maximum compactness and strength of methylcellulose-montmorillonite films and the highest X-ray diffraction peak were also attributed to 60 min. Using ultrasound radiation for the production of such films is strongly recommended. To obtain the

best quality and reach the required properties, considering the aim of the films, optimization of sonication time is mandatory.

Keywords Ultrasound time · Methyl cellulose · Film · Montmorillonite · Fourier transform infrared · X-ray diffraction

Introduction

Recently, composites such as polymer-layered silicate have become prevalent. Silicate layers should have at least one dimension of less than 100 nm [1–3]. Montmorillonite (MMT) is a type of silicate clay that has been widely used in polymer composites. High intercalation chemistry, strength, abundance in nature, low gas permeability, safety, and economic properties of MMT have led to the widespread use of this material [4–7].

Many investigations have shown that incorporating nano-scaled silicate layers into polymers increases their mechanical properties, heat, and moisture resistance, and decreases their moisture adsorption, permeability, and flammability [6, 8]. Depending on silicate dispersion, two types of composite, i.e., intercalated and exfoliated, can be obtained. The latter is known as delaminated silicate and is preferred to the former because of having better barrier and mechanical properties [7, 9, 10].

Producing clay composites can be achieved by four methods: in situ interactive polymerization, in situ synthesis, melt intercalation, and solution intercalation. Researchers have applied suitable blending methods, such as shear, high pressure, centrifuge, and ultrasonication mixing, for producing a high performance composite. Ultrasonication is one of the most important methods for increasing intergallery spacing between silicate layers and dispersing them in the polymers. Ultrasound treatment can

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help in terms of easily achieving exfoliated clay structure and increasing d-spacing in comparison to non-sonicated samples [11, 12]. Furthermore, ultrasonication widely affects the polymer itself, and as a result, changes composite properties. Therefore, power and time of sonication are critical and should be seriously considered in composite preparations [13–15]. Acoustic cavitations, bubbles, and their collapses are the main reasons for chemical reactions (sonochemistry) and physical changes in the substances which are exposed to ultrasound radiation. Bubble violent explosion generates extreme temperatures and pressures inside the bubbles and solvent. So, the materials in the solvent are disintegrated and several highly reactive radicals would be generated. Several chemical reactions can occur between these active radicals and substances in the medium. Finally, more chemical bonds, like H and covalent bonds will be generated [14, 16, 17].

Alshabanat et al. found that increasing sonication time in polystyrene resulted in the creation of crystalline structures in the amorphous region. The maximum peak intensity in X-ray diffraction (XRD) was obtained after 1 h of sonicating polystyrene-MMT composite, which showed higher interaction and chemical bonds with MMT [1]. Intergallery spacing of epoxy-clay composite increased with increasing sonication time at low clay loading (2%). Dispersion of MMT at high sonication times was significantly better. Increasing sonication time enhanced tensile strength, while hardness did not change [18]. Chen et al. revealed that 15 min ultrasound time could break cross-links between amylose and amylopectin in maize starch, which in turn caused depletion in opacity, water vapor permeability (WVP), and elongation in the films as well as increasing tensile strength (TS) [14]. Ultrasound and microwave combination, especially lower than 20 min, can significantly affect barrier and mechanical properties of the films from methyl cellulose (MC), wheat bran cellulose and soy protein [15, 19, 20]. To the best knowledge of the authors, there are not any reports that show and prove the effects of ultrasound time on biodegradable films like MC [21, 22].

The present research was designed to show and prove the relationship between sonication time and properties of methyl cellulose-montmorillonite (MC-MMT) films as well as to illustrate how time of sonication will affect the films properties. The research was also designed to show the importance of sonication time optimization.

Materials and methods

Materials

MC was prepared from Sigma Aldrich, 274429 (average molecular weight of 40000 and 2% solution viscosity of

400 cp) (PubChem CID: 44263857). MMT without any modifications was supplied from Southern Clay Products Inc., USA (Cloisite Na⁺). Glycerol (PubChem CID: 753) was purchased from Merck Company.

MMT preparation

MMT preparation is illustrated in Fig. 1.

Standard techniques used for MMT preparation

All the MMT preparations were carried out in 100-ml laboratory beakers. Stirrers and magnet stirring sets were Heidolf MR 3001 (Germany) and 2-cm magnet, respectively. In MMT and also in film preparations, a water bath sonicator was used (ULTRASONS-H, PSelectaCE95, 50 kHz, 1000 W). From the beginning to the end of the MMT preparation, the top of the beakers was wrapped tightly with a soft polyethylene sheet to avoid water vaporization.

Film preparation

Each polymer has individual characteristics and the method for its film preparation is exclusive. The process of film preparation is illustrated in Fig. 2.

Standard techniques used for film preparation

In the film preparation, stirrer and magnet stirring were Heidolf MR 3001 and 6-cm magnet, respectively. In the film preparation, a water bath sonicator was used (ULTRASONS-H, PSelecta CE95, 50 kHz, 1000 W). From the beginning to the end of the film preparation, 500-ml blue cap glass containers were used and tightly capped to avoid the solvent evaporation.

Properties of MC-MMT films

The MC-MMT films were characterized by mechanical properties (TS and elongation at break), opacity, WVP,

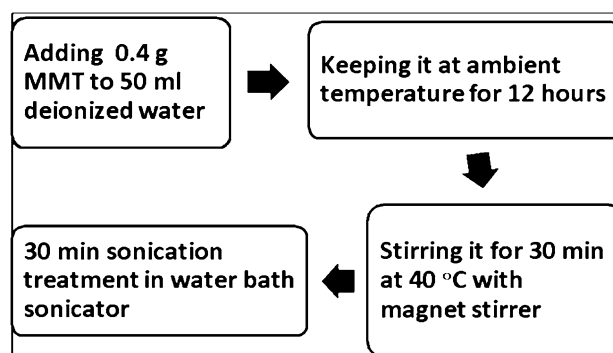
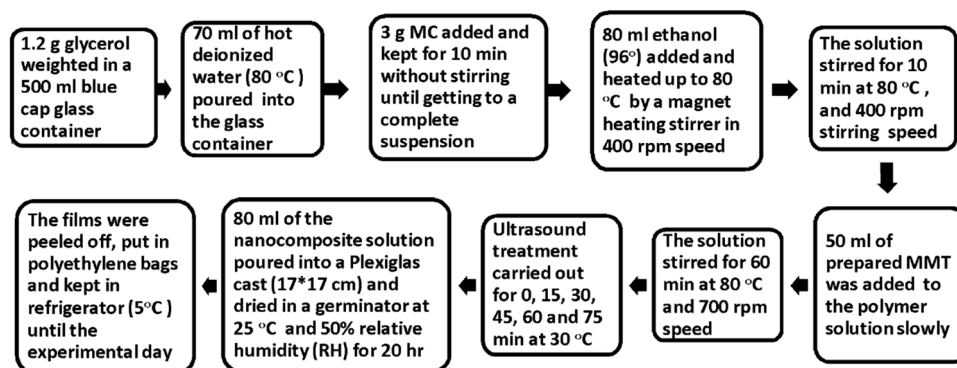


Fig. 1 MMT preparation for adding to MC solution



Fig. 2 Preparation of MC-MMT films

color, yellowness index (*YI*), and thickness. XRD was used to investigate the dispersion of MMT in MC polymer. Fourier transform infrared (FTIR) spectroscopy was applied to show chemical bonds and the interaction between MMT and MC/glycerol at different sonication times.

Mechanical properties

TS and elongation at break evaluations were performed using a Universal Testing Machine (Instron, Hounsfield H50KS, England) according to ASTM D882-12 [23]. Speed of upper Instron's jaw was 50 mm/min. Rectangular strips (8×1 cm) were cut from the film sheets and 2 cm from the top and bottom of the strips was carefully wrapped using adhesive paper scotch. The latter was done to avoid compression, rupture, and slipping of the films between the Instron's jaws. The distance between the jaws was 4 cm. The strips were equilibrated at 25 °C and 50% RH for 72 h before doing the test.

X-ray diffraction (XRD)

Exfoliate and intercalate structures of MC-MMT films were evaluated using X'PertMPD, Philips, Holland XRD, diffractometer equipped with CO K α 1.79 Å (scanning rate of 0.02°/S, scan step time of 2 s, voltage of 40 kv, and current of 30 mA). Collections of the data were performed at 2 θ angle from 1 to 12°. Using Bragg equation (Eq. 1), the XRD software calculated the d-spacing between the MMT layers. The most suitable, and popular method for calculating d-spacing of MMT in such films and proving the penetration of polymer into the MMT layers (Intercalate structure) is using Bragg equation. Disappearing MMT peak in the XRD spectra of the films, shows exfoliate structure [24, 25].

$$\lambda = 2d \sin \theta \quad (1)$$

Where, λ is the wavelength of the X-ray beam (nm), d is the spacing (nm) between the two layers, and θ (°) is the angle of incidence.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were collected using FTIR spectrometer (Nexus 6700, Thermo Nicolet, USA). Transmission method was applied to the MC-MMT films. IR absorption spectra of the MC-MMT films were obtained for the purposes of measuring and scanning. The spectral collections were performed in the wavenumber range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1} .

Wvp

The WVP evaluations were based on the modified ASTM E96/E96 M-14 method [26]. Before running the test, the circle samples ($19.625 \times 10^{-4} \text{ m}^2$ in the surface area) were cut and equilibrated at 25 °C and 50% RH for 72 h. Then, they were carefully placed and sealed using grease oil on the top of the glass cells ($7.065 \times 10^{-4} \text{ m}^2$ in internal surface area, $19.625 \times 10^{-4} \text{ m}^2$ in edge surface area, and 3.5 cm depth), which contained 8 ml of saturated NaCl (74% RH). To prevent the leakage of moisture through the seals, in addition to using grease oil, circle rubber rings were put on the films as well as on the edges of the cells and tightly gripped by four metal clamps. The glass cells were put in a desiccator containing 800 g of silica gel and kept at 25 °C and 50% RH. The cells were weighed every 5 h for 72 h. WVP was calculated by Eq. (2).

$$WVP = \frac{\Delta m \times X}{A \times \Delta t \times \Delta p} \quad (2)$$

Where *WVP* is water vapor permeability (g/m h KPa), Δm is the total weight loss of the cells (g), *X* is the thickness of the films (*m*), *A* is internal or exposed area of the film (m^2), Δt is the time of vapor penetration (*h*), and Δp is the pressure gradient ($\text{dp} = 2.368 \text{ Kpa}$ was calculated using a psychrometric chart from Universal Industrial Gases, Inc, Pennsylvania, USA).



Table 1 Optimization conditions and selected sample

Name	Goal	Lower limit	Upper limit	Importance	Selected sample with 90.5% desirability
Ultrasound time	Is in range	0	75	3	60 min
Tensile stress	Maximize	40	69.35	3	66.92 MPa
Elongation	Is in range	22.8	45.5	3	36.7%
WVP	Minimize	0.51	0.82	5	0.56×10^{-3} g/m h KPa

Optical evaluations

Color

L^* , a^* , and b^* (mode of CIE) parameters of the MC-MMT films were measured in a tristimulus colorimeter (ColorFlex EZ, Bench top Spectrophotometers, USA). Five replicates were performed for each sample [27].

Yi

YI, which shows yellowish color of the films, was measured according to ASTM standard E313-15 [28]. Equation (3) was used for YI calculation.

$$YI = ((Cx.X - Cz.Z)/Y) \times 100 \quad (3)$$

Where XYZ are tristimulus factors, measured by a tristimulus colorimeter (ColorFlex EZ, Bench-top Spectrophotometers, USA), and Cx and Cz are constants obtained from ASTM standard E313-15.

Opacity

Opacity of the MC-MMT films was measured using a Cary 60 UV/VIS spectrophotometer. Rectangular pieces (8×1 cm) of the films were prepared and put in the sample position of the spectrophotometer. Empty measurement was used as the reference. The opacity of the films was calculated using Eq. (4) [6, 27, 29].

$$Opacity = \frac{Abs_{600}}{X} \quad (4)$$

Where Abs 600 is absorbance at 600 nm and X is the thickness (mm) of the films.

Thickness

Using a hand micrometer, the thickness of the MC-MMT films was measured (Mitutoyo, Model 0052526, Japan). Five locations of the films were evaluated and the average value was used for each sample.

Statistical design

The MC-MMT films were produced in a completely randomized design (CRD). The treatments were: 0 min time of sonication as control (MC 0), 15 min (MC 15), 30 min (MC 30), 45 min (MC 45), 60 min (MC 60), and 75 min (MC 75). Design Expert ver. 7.0 was used for optimization. Using numerical optimization, the goals for each response were set then the software generated optimal conditions (Table 1). Data were analyzed mainly by SPSS20 software and where needed other statistical softwares such as MSTATC and Design Expert ver. 7.0 were also used. Multiple range Duncan test was performed for mean comparisons ($\alpha = 0.05$). All the experiments and measurements were done with at least three replications.

Results and discussion

Mechanical properties

Time of sonication remarkably affected tensile strength ($p < 0.01$), while it did not have any significant effect on elongation ($p > 0.05$). After 60 min, tensile strength and elongation reached 66.92 MPa and 37%, respectively. Compared with the control sample, there was 43.7% enhancement for tensile strength (Fig. 3). Rimdusit et al. [30] reported that tensile strength and elongation of MC-MMT films (10% MMT) were 92 MPa and 19%, respectively. Dobrovol et al. [22] announced tensile strength and elongation of MC-MMT films (10% MMT) around 137 MPa and 22%, respectively [22, 30]. Due to the presence of glycerol in this research, tensile strength and elongation were lower and higher than the other researches, respectively.

Tensile strength decreased after 15 min of sonication (Fig. 3). The viscosity of the MC polymer solution was high; so, low time of sonication not only could increase the film's strength, but also could diminish it. In addition, 15 min of sonication was not sufficient for generating radicals and their interaction with polymer and other



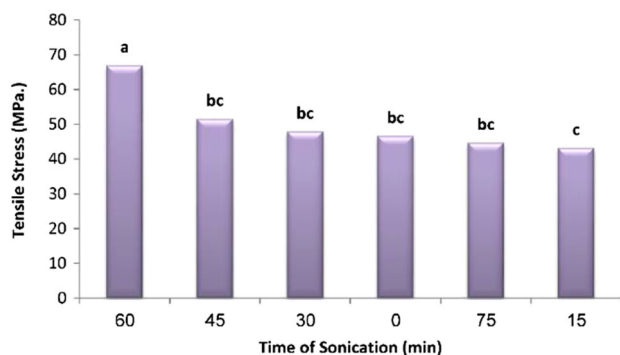


Fig. 3 Comparing tensile strengths of MC-MMT films at different times of sonication. Different letters show significant differences ($p < 0.05$)

materials in the solution. On the other hand, probably some of the bonds of the polymer were decomposed at the 1st min of sonication; as a result, tensile strength was decreased. The results proved that time of sonication is critical and should be optimized.

Increasing time of sonication improved tensile strength up to 60 min, while it decreased at 75 min (Fig. 3). If sonication time and intensity had more increase, the polymer and its chemical bonds would be probably decomposed and adversely affect mechanical properties, like what was seen at 75 min of sonication time. Several researchers have evaluated the effect of ultrasound radiation on different film properties and observed that tensile strength is improved, while different results are obtained about elongation [14, 15, 31].

If the solvent is water, active H and OH radicals and hydrogen peroxide will be usually generated. Several chemical reactions occur between these active radicals and substances in the medium, like MC, MMT, and glycerol in this study. Finally, more chemical bonds, like H and covalent bonds, will be generated. Furthermore, sonication causes the exit of air bubble from the solution, which in turn results in more compact films with higher strength and resistance toward elongation [14]. All these mechanisms could be the reasons for improving tensile strength at higher sonication time in MC-MMT films. We can conclude that the compactness of the films, chemical bonds, and their intensity at 60 min were higher than that of the other treatments.

Wvp

The effect of sonication time on WVP of MC-MMT films was significant ($p < 0.05$). Minimum WVP was related to 60 min of sonication time (0.56×10^{-3} g/m h KPa). The data showed that 60 min of sonication could decrease 21.35% of WVP in comparison to the control. Figure 4 shows the decreasing trend and mean comparisons of

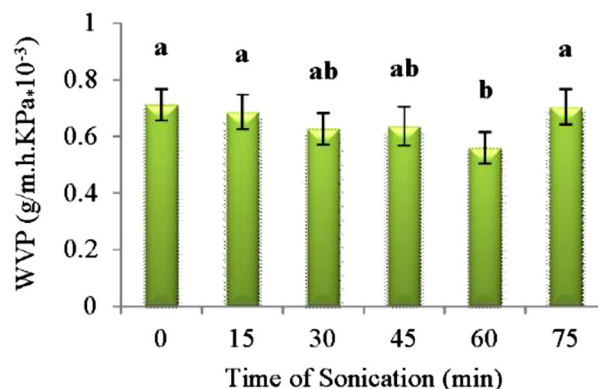


Fig. 4 Comparing WVP of the MC-MMT films at different sonication times. Different letters show significant differences ($p < 0.05$)

WVP. As was completely described in the previous sections, the most compact film was obtained at 60 min. So, water vapor could not easily pass through such a film. Other researchers have reported similar results [14, 19]. There was not any direct report about WVP of MC-MMT films in other papers, while Turhan and Sahbaz [32] reported WVP of MC films (without MMT) around 0.4×10^{-3} g/m h KPa, which was nearly like the obtained result in present research [32]. Yu et al. [33] announced that WVP of carboxymethylcellulose films with 4% MMT was 0.8×10^{-5} g/m h KPa. The difference of the basic polymers and the presence of glycerol are the main reasons of higher WVP in present study.

Optimization

Optimization analysis by Design Expert showed that 60 min of sonication time was the optimum treatment (with 90.5% desirability) for using the films in food packaging. According to the results of mechanical and WVP properties and as the 60 min treatment was optimum, other properties (XRD, FTIR, and Optical) were evaluated at 45, 60, and 75 min. Optimization conditions are depicted in Table 1.

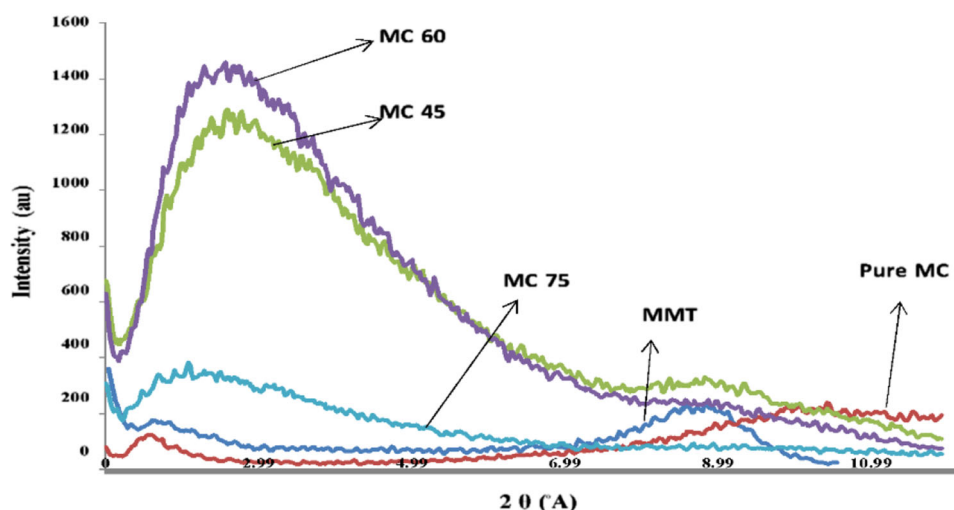
XRD

At the first glance on XRD graphs of MC-MMT films (Fig. 5), it can be found that the films had an intercalated structure, since the peak angle of MMT decreased from 8.7 (pure MMT) to nearly 2 Å. If MMT structure in the films was exfoliated, we could not see any peak in XRD spectrum [6, 34].

Increasing ultrasound time caused the enhancement of d-spacing between MMT layers in the MC-MMT films, and this shows the penetration of MC into the d-spacing of MMT layers and intercalated structure. Data calculation by Eq. 1 showed that increasing time of sonication from 45 to



Fig. 5 XRD of MC-MMT films at different sonication times



75 min increased d-spacing from 3.88 to 4.83 nm, while peak angles decreased from 2.64 to 2.12°. Therefore, incorporation of MC and glycerol into the d-spacing of MMT layers was increased by increasing time of sonication [6, 11, 34].

There are some relatively small (sodium) ions in the interlayers of MMT and these ions can be exchanged with onium cations in the polymer (MC)/glycerol. This ion-exchange reaction results in widening the gap between the single sheets, enabling polymer chains to move in between them and the surface properties of each single sheet are changed widely [1, 35]. As explained in FTIR section MC does not have high compatibility with MMT because of the presence of low hydrophilic ions. Therefore, MC showed low interaction with MMT, while glycerol had high interaction with MMT and created high new bonds (Fig. 6). These facts provide evidences for the penetration of MC into the intergallery space of MMT sheets and increasing d-spacing.

Intensity/height of the XRD peaks shows the dispersity of MMT layers in the polymers. The lower intensity of the peaks had more scattering of MMT and the height of XRD peaks was noticeably different (Fig. 5). Since the viscosity of the MC solution was high, ultrasound and probably new chemical bonds played significant roles in MMT dispersing. The height of the peak in the 75 min treatment was considerably lower than that of the others, which showed that 75 min of sonication could decompose polymer chains along with decreasing consistency, and as a result, MMT layers were widely dispersed in the medium. As can be observed in the mechanical properties, the generated bonds at the 60 min of sonication were higher than those of the other treatments. So, the medium (matrix) became more consistent and MMT scattering in this medium grew less than the other treatments, even lower than 45 min. Alshabanat et al. [1] reported nearly the same results. Results of

this study represented less consistency and polymer cross-linking for 45 min of ultrasound treatment. Tensile strength, WVP, and FTIR spectra verified the XRD results.

FTIR spectroscopy

The ultrasound treatments had remarkable and wide effects on the MC-MMT films. The FTIR spectra for MC-MMT films at different sonication times are shown in Fig. 6 and Table 2. At high wave numbers, control MC-MMT films (MC 0) had absorption bands related to O–H stretching at 3450, 3251 and 3138 cm^{-1} . By applying 45 min of sonication and increasing time to 60 and 75 min, the O–H stretching bands, 3450 and 3251 shifted to lower wave numbers, while 3138 shifted to higher wave numbers (Fig. 6). These values were nearly consistent with those reported by Rimdusit et al. [30] and Pandey [36]. In addition to shifting and emerging new peaks, the intensity of peaks, especially in 60 and 75 min increased and got sharper obviously.

In low wave numbers, control MC-MMT films (MC 0) had absorption peaks related to C–C stretching, C–H rock and C–O stretching at 1431, 1356 and 1159, respectively. These bands shifted to lower wave numbers by applying 45 min sonication, while these bands disappeared at 60 and 75 min and new peaks emerged (Fig. 6). These values are again reported by Rimdusit et al. [30] and Pandey [36].

Control MC-MMT films had a band at 1099 related to Si–O Stretching. Applying 45 min sonication and increasing it to 60 and 75 min shifted this peak to lower wave numbers. According to the reports of Tzavalas and Gregoriou [37], we can attribute these peaks to the alteration of environment of the Si atoms (in MMT) due to the presence and penetration of polymer and alkyls between MMT layers. Higher intensities of these peaks show the progress of intercalation in films.



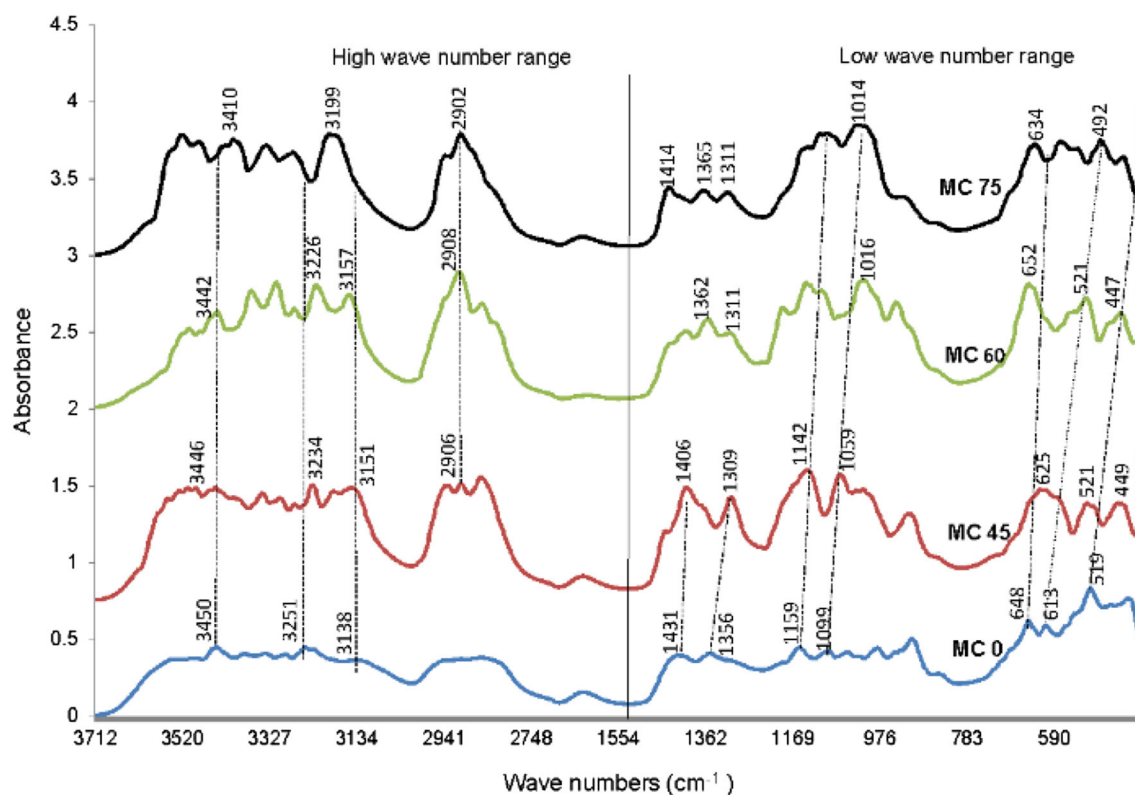


Fig. 6 FTIR spectra of MC-MMT films

Table 2 Infrared spectra absorption data of MC-MMT films at different times of sonication

Range of high wave number				Assignments	Range of low wave number				Assignments
MC 0	MC 45	MC 60	MC 75		MC 0	MC 45	MC 60	MC 75	
3450	3446	3442	3410	O–H Stretch	1431	1406	O,N	O,N	C–C Stretch
3251	3234	3226	3199	O–H Stretch	1356	1309	O,N	O,N	C–H Rock
3138	3151	3157	3199	O–H Stretch	1159	1142	O,N	O,N	C–O Stretch
O	2906	2908	2902	C–H Stretch	1099	1059	1016	1014	Si–O Stretch
					648	625	652	634	C–H Bend
					613	O	521 N	492 N	C–H Bend
					519	494	447	O	C–H Bend

O omitted peaks, N new peaks

As can be seen in Fig. 6 control MC-MMT film had 648, 613 and 519 bands related to C–H bends. These bands changed widely by applying ultrasound and increasing its time (Table 2). These bands are called fingerprint region and assigning them are difficult, for example, Alshabanat et al. [1] assigned 528 and 466 as Si–O asymmetric bending in MMT.

Overall, by applying ultrasound to the MC solution and increasing time, chemical bonds changed outstandingly (Table 2). Some of the peaks shifted positively and some negatively and most of them got sharper with higher intensity, showing that the polymer/glycerol was

incorporated into the intergallery space of the MMT layers and new chemical bonds were formed [1, 37, 38]. By increasing time of sonication up to 60 min, fewer changes occurred at low wave numbers, while at high wave numbers, peaks got wider and sharper (Fig. 6). In addition, 75 min of ultrasound made more changes in the peaks at both low and high wave numbers, representing that high ultrasound times caused changes in the polymer bonds and as a result in the film properties. Depending to the aim of using the films, these changes might be useful or not. So, to get the best quality, preparation of the films should be optimized in terms of sonication time.



Table 3 Comparisons of optical properties of MC-MMT films

Thickness				
Ultrasound times (min)	b^*	YI	Opacity ($\times 10^{-4}$)	L^*
45	3.37 ± 0.04^b	5.3169 ± 0.11^{ab}	12.051 ± 1.059^b	90.81 ± 0.07^b
60	3.475 ± 0.02^a	5.7721 ± 0.18^{ab}	17.072 ± 1.23^a	90.66 ± 0.01^c
75	3.265 ± 0.02^c	4.9564 ± 0.19^c	10.609 ± 1.83^b	91.035 ± 0.02^a

Different letters show significant differences ($p < 0.05$)

Values are mean \pm standard deviation

Optical properties of MC-MMT films

Opacity is one of the most important features of films, especially for food packaging. Ultrasound time had a significant effect on the opacity of the MC-MMT films ($p < 0.05$). In addition, 60 min of sonication had the highest opacity (0.0017) in the films (Table 3).

Analysis of variance showed that time of sonication had no significant effects on a^* (redness) factor of the MC-MMT films, while it significantly affected L^* (lightness) and b^* (yellowness) factors ($p < 0.01$) as well as YI ($p < 0.05$). Maximum opacity, YI , and b^* of the films and minimum L^* were attributed to 60 min of sonication (Table 3). Color and YI results verified opacity feature of the films, which was very low at 60 min. Formation of more chemical bonds and more exit of air bubbles from the polymer solution at 60 min resulted in more compactness of the film [14]. Therefore, transmittance would be decreased in such a film. Tensile strength, FTIR, and WVP results were in accordance with the optical properties.

Rodriguez et al. [39] reported that b^* of cellulose acetate with 7.5% MMT was 1.6 and Yu et al. [33] announced that the b^* of carboxymethylcellulose with 8% MMT was 0.09, while in present research the maximum b^* (3.475; 60 min) was outstandingly higher than the other reported values. Tunc and Duman [6] reported the opacity of MC-MMT films (with 20% MMT) around 6.7. The reason of lower opacity in this study (1.7, when thickness is in micron) is applying lower MMT content (13%) in the films. Rodriguez et al. [36] and Yu et al. [33] reported the opacity of cellulose acetate and carboxymethylcellulose films 2.81 and 2.18, respectively [6, 36, 39]. The kind of polymer, MMT content, and the method of film preparation are the reasons of these differences.

The average thickness of the MC-MMT films was 64.48 μ . Times of sonication did not significantly affect the thickness of the films ($p < 0.05$).

Conclusion

Sonication time remarkably affected the properties of the MC-MMT films. Emerging new bonds between polymers and nanomaterials, increasing intensity of them, and more

dispersion of nanomaterial in the polymer are the effects of sonication time. Because of these effects, properties of the films will change widely. With an increase in sonication time tensile strength (46.57–66.92 MPa), opacity (12.05–17.07), b^* factor (3.33–3.475), and YI (5.3–5.8) increased outstandingly up to 60 min, while continuing sonication resulted in the depletion of these traits. On the contrary, L^* factor (90.81–90.66) and WVP (0.66 – 0.56×10^{-3} g/m h KPa) decreased by increasing time of sonication up to 60 min. The results of XRD and FTIR verified the effects of sonication time on the film properties. Our results presented in this report suggest that for achieving desirable quality of the films, time of sonication must be optimized. Showing, proving, and verifying the importance of sonication time by FTIR and XRD were illustrated in this paper.

Acknowledgements This work was done by the support of Tarbiat Modares University, as a part of a PhD dissertation. So, we gratefully appreciate their kind cooperation. In addition, we sincerely acknowledge the technicians of Food and Central Laboratories in College of Agriculture.

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